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(54) IMPROVEMENTS RELATING TO PHOTO-RESISTS

(71) We, E. I. Du Pont De Nemours and Company, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the production and use of photo-resists.

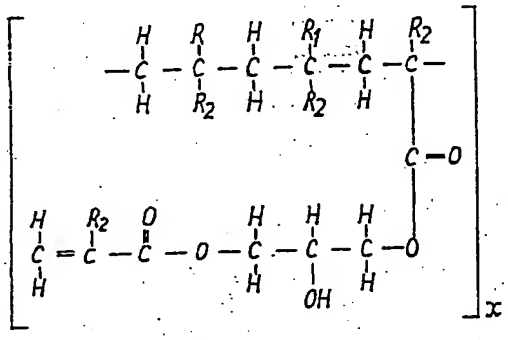
Various processes and elements have been proposed for producing photoresists. Conventionally, photoresists have been produced using gelatin silver halide photographic emulsions or gelatin layers containing potassium dichromate as the light-sensitive agent. Such layers are imagewise exposed and developed with special solutions and/or warm water. Gelatin and other water-soluble colloid layers have many disadvantages for use as photoresist layers. It is inconvenient to use repeated liquid treatments. In addition water-soluble colloid layers, even though they have become substantially water insolubilized during treatment, are not resistant to moisture. Synthetic binders for light-sensitive silver halide and chromium salts have also been proposed but these, too, require liquid treatments to form the image resist and it is difficult to properly harden such various polymer synthetic materials which are gellable by the action of light.

In these cases, the synthetic material is applied to the metal or other permanent surface as a liquid coating and then exposed to light either in a liquid gellable state or in a dry state. The coating is done by dipping, whirling or roller coating. This is inconvenient in many cases because of the requirement that either the support., e.g. metal, must be coated at the point of manufacture of the resist composition, or the composition must be shipped to the user of the resists who must then coat the composition. These piece by piece operations are generally wasteful of resist composition and produce coatings of marginal quality and uniformity. Either procedure has many obvious disadvantages. One of these is that liquid coatings are applied to perforated circuit boards in certain cases where electroplating is to be done, and connections made through the perforations often cause difficulty. Another disadvantage is that the preparation of photoresists by the above processes involves long drying times by the user and a high risk that dirt will settle on the coating during the drying.

In Patent Specification No. 1,128,850 we describe and claim a process for the localised permanent modification of a solid surface in predetermined areas only which comprises the step of laminating at a temperature up to 150°C directly to the surface a dry, flexible photosensitive layer which is coated on a flexible polymeric film support towards which it has low to moderate adhesion, the photosensitive layer consisting of photodimerizable composition, a polymer sensitized with a diazonium compound or azide, or a photopolymerizable composition comprising

(a) a polymer having the formula;

[*Price 25p*]



where R and R_1 are each —CN, $-\overset{O}{\overset{\|}{C}}-OR_3$ or pyrrolidone, R_3 is an alkyl group of 1 to 18 carbon atoms, R_2 is H or CH_3 and x is a positive integer of 10 to 1000, and

(b) an addition polymerisation initiator activatable by actinic light; exposing the photosensitive layer imagewise to actinic radiation to form a polymer image or cross linked polymer image therein either before or after removing the support from the layer, removing the unexposed areas of the photosensitive layer by means of a liquid to leave a resist image on the solid surface and subjecting the surface carrying the resist to an etching or plating treatment whereby the unprotected areas thereof are permanently modified.

We have now found that the process described in Patent Specification No. 1,128,850 can be modified by using other photopolymerisable compositions which can give operational advantages over the photopolymerisable composition whose use is described and claimed in Patent Specification No. 1,128,850.

Accordingly, the present invention provides an improvement in or modification of the process described in Patent Specification No. 1,128,850 and comprises a process for the localised permanent modification of a solid surface in predetermined areas only which comprises laminating at a temperature up to 150°C. directly to the surface a dry, flexible photosensitive layer which is coated on a flexible polymeric film support towards which it has low to moderate adhesion, the photosensitive layer consisting of a photopolymerisable composition comprising an addition polymerisation initiator activatable by actinic light and a photopolymerisable compound which contains less than 10 ethylenically unsaturated groups per molecule, exposing the photosensitive layer imagewise to actinic radiation to form a polymer image therein either before or after removal of the support from the photosensitive layer, removing the unexposed areas of the photosensitive layer by means of a liquid to leave a resist image on the solid surface and subjecting the surface carrying the resist image to an etching or plating treatment whereby the unprotected areas thereof are permanently modified.

The ethylenically unsaturated groups preferably are vinyl or α-methyl vinyl groups and it is preferred to use photopolymerisable compounds containing from 1 to 6 acrylate or methacrylate ester groups. Such compounds may be derived from polyhydric alcohols such as alkylene glycols, polyalkylene glycols, pentaerythritol or dipentaerythritol by esterification with acrylic or methacrylic acid or an ester-forming derivative thereof.

It is not essential that the photopolymerisable compound contain more than one ethylenically unsaturated group in the monomer molecule and, as examples of suitable photopolymerisable compositions containing monoethylenically unsaturated compounds, reference may be made to compositions containing:

(a) 30 parts by weight styrene, 70 parts by weight of a commercial polyester which is a viscous relatively low molecular weight polypropylene glycol/maleate/phthalate and 1 part by weight benzoin methylether;

(b) 55 parts by weight methylmethacrylate, 20 parts by weight polymeric methylmethacrylate, 25 parts by weight monomeric polyethylene glycol dimethacrylate and 1 part by weight benzoin; and

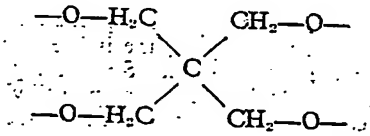
(c) 19 parts by weight methylmethacrylate, 28 parts by weight polymeric methylmethacrylate, 25 parts by weight monomer polyethylene glycol dimethacrylate, 1 part by weight benzoin and 27 parts by weight of silica.

This last mentioned photopolymerisable composition may be prepared by mixing 19 parts by weight of methylmethacrylate, 28 parts by weight of polymeric methyl-

methacrylate, 25 parts by weight of monomeric polyethylene glycol dimethacrylate and 1 part by weight of benzoin to give a syrup. To this syrup are added 25 parts by weight of a specially prepared low density hydrophobic silica having particles no greater in size than 1 micron and an appreciable proportion less than 0.1 to 0.01 micron, and the resulting mixture is compounded on a three roll mill to obtain a sticky mass which is converted to a stiff putty on addition of 2 more parts by weight of silica.

Other useful photopolymerisable compositions can be derived from alkylene and polyalkylene glycol diacrylates prepared from an alkylene glycol of 2 to 15 carbon atoms or a polyalkylene ether glycol of 1 to 10 ether linkages, and those disclosed in our Specification No. 807,948, e.g. those having a plurality of addition polymerisable ethylenic double bonds, particularly terminal double bonds, and especially those wherein at least one and preferably most of such double bonds are conjugated with a doubly bonded carbon, including carbon doubly bonded to carbon and to such hetero-atoms as nitrogen, oxygen and sulphur. Outstanding are such materials wherein the terminal ethylenic double bonds are conjugated with ester or amide structures. The following specific compounds are illustrative: unsaturated esters of alcohols, preferably polyols and particularly such esters of the alphamethylene carboxylic acids, e.g. ethylene diacrylate, diethylene glycol diacrylate, glycerol-1,3-diacrylate, glycerol triacrylate, ethylene dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, 1,4-benzenediol dimethacrylate, pentaerythritol triacrylate and trimethacrylate, pentaerythritol tetracrylate and tetramethacrylate, dipentaerythritol hexacrylate, 1,3-propanediol diacrylate, 1,5-pentanediol dimethacrylate, the bis-acrylates and methacrylates of polyethylene glycols of molecular weight 200—1500, unsaturated amides, particularly those of the alpha-methylene carboxylic acids, and especially those of alpha, omega-diamones and oxygen-interrupted alpha, omega-diamines, such as methylene bis-acrylamide, methylene bis-methacrylamide, ethylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, diethylene triamine trismethacrylamide, bis-(gamma-methacrylamidopropoxy)ethane, beta-methacrylamidoethyl methacrylate, N-(beta-hydroxyethyl)-beta-(methacrylamido)ethyl acrylate and N,N-bis-(beta-methacrylyloxyethyl)acrylamide; vinyl esters such as divinyl succinate, divinyl adipate, divinyl phthalate, divinyl terephthalate, divinyl benzene-1,3-disulphonate, and divinyl butane-1,4-disulphonate; styrene and unsaturated aldehydes, such as sorbaldehyde (hexanedienal). An outstanding class of these preferred addition polymerisable components are the esters and amides of alpha-methylene carboxylic acids and substituted carboxylic acids with polyols and polyamides wherein the molecular chain between the hydroxyls and amino groups is solely carbon or oxygen-interrupted carbon. The preferred monomeric compounds are difunctional, but monofunctional and polyfunctional monomers can be used.

The esters of pentaerythritol mentioned above, and particularly pentaerythritol triacrylate, represent one of the more preferred classes of photopolymerisable compound for use in accordance with the present invention. A preferred class of pentaerythritol derivative for use in the practice in the present invention may be represented by the general formula:



wherein two or three of the free bonds having attached thereto an acrylyl radical and the remaining free bond or bonds are linked to an aliphatic hydrocarbon radical, an ether substituted aliphatic hydrocarbon radical or a carboxylic acid ester substituted aliphatic hydrocarbon radical, any of which may carry a free hydroxyl radical or hydrogen. When such pentaerythritol derivatives are used in the photopolymerisable compositions it is desirable to incorporate in the composition a thermoplastic macromolecular organic polymer solid at 50°C.

Pentaerythritol compounds falling within the above general formula include compounds having the following structure:

$$(ROCH_2—)_p G(CH_2—OH)_m(CH_2—OOCH=CH_2)_n$$

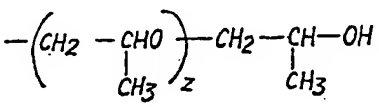
wherein n is either 2 or 3; m is 0, 1 or 2; p is 0 or 1; and m+n+p equals 4; R is alkyl of 1—4 carbons, e.g. methyl, ethyl, n-propyl, n-butyl, isopropyl; hydroxyalkyl

of 2—4 carbons, e.g. 2-hydroxyethyl, 3-hydroxy-n-propyl, 4-hydroxy-n-butyl; dihydroxy-alkyl of 3 to 4 carbons, e.g. 2,3-dihydroxy propyl, and

(1) groups of the formula:

$$-(CH_2CH_2O)_x-CH_2CH_2OH$$

where x=1 to 5;
and groups of the formula:



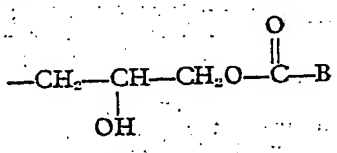
where z=1 to 5.

(2) groups of the formula:

$$-(CH_2CH_2O)_yCH_3$$

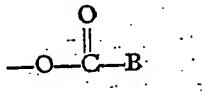
where y=1 to 15;

(3) groups of the formula:



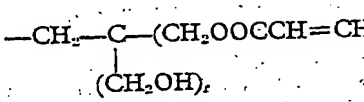
where B=methyl, vinyl, ethyl or n-propyl;

(4) hydroxy-alkyl groups described above, where some or all of the groups are replaced by



where B=methyl, vinyl, ethyl or n-propyl;

(5) groups of the formula:



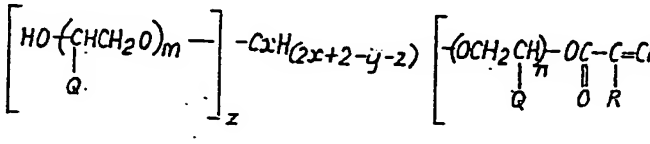
where s=0, 1, 2 or 3, and s+r=3.

Particularly useful monomers of these classes are pentaerythritol diacrylate and triacrylate; dipentaerythritol tetraacrylate, pentaacrylate and hexaacrylate; 2,2,2,2′-tetraacrylyloxymethyl-2′-hydroxydiethyl ether; 2,2,2,1′-tetraacrylyloxymethyl-2′-hydroxydiethyl ether and 2,2,2-triacrylyloxymethyl-2′-hydroxydiethyl ether.

Suitable thermoplastic polymers for use in the photosensitive composition include: (a) copolyesters, e.g. those prepared by the reaction of a polymethylene glycol of the formula $HO(CH_2)_nOH$, wherein n is a whole number 2 to 10 inclusive, with (1) mixtures of hexahydroterephthalic, sebacic and terephthalic acids, (2) mixtures of terephthalic, isophthalic and sebacic acids, (3) mixtures of terephthalic and sebacic acids and (4) mixtures of terephthalic and isophthalic acids, or prepared by reaction of mixture of said glycols with (i) mixtures of terephthalic, isophthalic and sebacic acids and (ii) mixtures of terephthalic, isophthalic, sebacic and adipic acids, (b) nylons or polyamides, e.g. N-methoxymethyl polyhexamethylene adipamide; (c) vinylidene chloride copolymers, e.g. vinylidene chloride/acrylonitrile, vinylidene chloride/methacrylate and vinylidene chloride/vinylacetate copolymers; (d) cellulose ethers, e.g. methyl cellulose, ethyl cellulose and benzyl cellulose; (e) polyethylene, (f) synthetic rubbers, e.g. butadiene/acrylonitrile copolymers, and 2-chloro-1,3-butadiene polymers; (g) cellulose esters, e.g. cellulose acetate, cellulose acetate succinate and cellulose acetate butyrate; (h) vinyl ester polymers and copolymers, e.g. polyvinyl acetate/acrylate, ethylene/vinyl acetate copolymers, polyvinyl acetate/methacrylate and polyvinyl acetate; (i) polyacrylate and alpha-alkyl polyacrylate esters, e.g. polymethyl

methacrylate and polyethyl methacrylate; (j) high molecular weight polyethylene oxides or polyglycols having average molecular weights from about 4,000 to 1,000,000; (k) polyvinyl chloride and vinyl chloride copolymers, e.g. vinyl chloride/vinyl acetate copolymer; (e) polyvinyl acetals, e.g. polyvinyl butyral, polyvinyl formal; (m) polyformaldehydes; (n) polyurethanes; (o) polycarbonates; and (p) polystyrenes.

A still further class of ethylenically unsaturated compound that can be used in the photopolymerisable compositions in accordance with the present invention comprises monomeric branched chain polyol polyether polyesters of alpha-methylene carboxylic acids of 3 or 4 carbon atoms represented by the following formula:



wherein Q is H, CH_3 or C_2H_5, R is H or CH_3, x is 3, 4, 5 or 6, and is equal to or greater than y+z, y is 2, 3, 4, 5 or 6, z is 0, 1, 2, 3 or 4 and y+z is greater than 2, m is 0, 1 or a higher number, n is 1 or a higher number, and ny+mz is greater than 6 but not greater than 500.

Compounds of this general formula include the triacrylate and trimethacrylate esters of the reaction product of trimethylolpropane and ethylene oxide; the triacrylate ester of the reaction product of trimethylolpropase and propylene oxide; and the tetraacrylate and tetramethacrylate ester of the reaction products of ethylene oxide and propylene oxide with pentaerythritol. The reaction products preferably have an average molecular weight from about 450 to about 40,000.

When these polyester compounds containing from 2 to 6 ethylenically unsaturated groups are used in photopolymerisable compositions in accordance with the present invention, it is desirable that the composition contain a thermoplastic macromolecular organic polymer solid at 50°C. Suitable thermoplastic polymers include those indicated above as suitable for use with the pentaerythritol derivatives.

The surface which is to be modified in accordance with the present invention is preferably of an inorganic material, such as metal e.g. copper or anodized aluminium, or glass.

After exposure of the photopolymerisable composition and removal of the unexposed areas of the composition from the surface, the surface is permanently modified by etching or plating. Thus it can be treated with a suitable etchant to form an etched surface, or metal plate. If desired, after modification of the surface, the resist image can be removed from the surface by scraping or by means of a suitable solvent or with additional mechanical action, e.g. by force spraying, rubbing, brushing and/or abrading or by a combination of two or more of these means, but it is to be understood that the step of removing the resist, i.e. the exposed and polymerised portion of the photopolymerisable layer, does not form an essential step in the present invention.

In the event that the polymeric support material is opaque to radiation to which the photopolymerisable layer is sensitive, it is necessary to remove the polymeric support before exposure of the photopolymerisable layer, but if the support is transparent to the polymerising radiation, and it is preferred that the support should be so transparent, the support can be stripped from the photo-sensitive layer before or after its exposure as convenient.

In certain circumstances, it may be most convenient to laminate the photopolymerisable composition to the surface to be modified immediately prior to exposure and surface modification, and in these circumstances it is preferred to provide on the photopolymerisable layer a protective cover film which is removed immediately prior to laminating the photo-sensitive layer to the surface to be modified.

The thickness of the photo-sensitive layer to be laminated to the surface to be modified is preferably 0.003 to 0.08 mm. and the thickness of the support and optional protecting cover sheet is preferably 0.006 to 0.13 mm. As mentioned above, the support is preferably transparent to the actinic radiation that will bring about polymerisation of the photopolymerisable compound and it should also have good strength, dimensional stability to temperature changes and be resistant to solvent action by common solvents. The support must be chosen so that, at best, there is only a moderate amount of adhesion between the photopolymerisable coating and the support so that the latter can be readily stripped in dry condition from the photopolymerisable layer.

If a protecting cover sheet is used, it should have a lesser degree of adhesion to

the photopolymerisable layer than the support has to the photopolymerisable layer. This protecting sheet can be applied by pressing or laminating, e.g. by passing the sheet and coated element between rolls.

It is necessary that the photopolymerisable compositions contain addition polymerisation initiators that are activatable by actinic light and it is preferred to use for this purpose polynuclear quinones having two intracyclic carbonyl groups attached to intracyclic carbon atoms in a conjugated carbocyclic ring system. The preferred photoinitiators are disclosed in U.K. Patent Specification No. 843,238.

In addition to photo-initiators, other ingredients such as plasticizers, thermal inhibitors, colorants or fillers may be present.

In a preferred embodiment of the invention an element containing an image yielding photopolymerisable layer is made by coating a layer containing one of the photopolymerisable compounds mentioned above onto a suitable transparent film support.

The composition is coated to give a dry coating thickness of about 0.008 mm., although this may be varied readily, preferably between 0.003 mm. to 0.08 mm. After drying the layer, there is laminated to the surface thereof a removable cover film. A suitable film support may be chosen from a wide variety of films or foils composed of polymers, e.g. polyamides, polyolefins, polyesters, vinyl polymers, and cellulose esters and may have a thickness given above. If exposure is to be made before removing the support film, it must of course, transmit a substantial fraction of the actinic radiation incident upon it. If the support film is removed prior to exposure, no such restrictions apply. A particularly suitable film is a transparent polyethylene terephthalate film having a thickness of 0.003 mm. Suitable removable cover films, if used, may be chosen from the same group of high polymer films described above and may have a thickness in the same wide range, although the cover sheet can be thinner than the support with which it is used and should not be made of the same film. A cover film of 0.003 mm. thick polyethylene is especially suitable. Support and cover films as described above provide good protection to the resist layer. To apply the resist to, for example, a rigid copper-clad fiber-glass support to be used as a printed circuit, the cover film, if used, is stripped from the element and the resist layer on its supporting film is then laminated with heated resilient pressure rolls to the copper surface of the rigid support. This provides a sensitized surface ready immediately for exposure but still protected from dirt, lint and abrasion by virtue of the original support film. To product a resist image the element is exposed imagewise, preferably through the support film, and the support is then peeled off and the exposed resist developed by washing away the unexposed areas with solvent. The result is a rigid support bearing a relief resist image on its surface. The element is then subjected to plating or etching.

The process of this invention has many advantages. It eliminates the special coating and drying requirements imposed on users of the resists in applying liquid coatings to individual pieces to be imaged. The invention offers a simple and easy method of rapidly applying a highly uniform resist material to a surface to be imaged. A surface can be sensitized and ready for exposure in seconds as opposed to minutes or hours for the methods of forming resists which involve coating and drying at the site of use. In addition, the sensitized surface can be completely protected from dirt and abrasion by virtue of the fact that the original support film acts as a protective cover sheet after the resist element is applied to the surface to be imaged. Development is readily carried out and, if a dyed resist film is used, produces a dyed image directly without a separate dyeing operation. Dyed layers also facilitate inspection at any stage of the process. The photoresist layers sandwiched between two polymeric films after manufacture can easily be stocked as inventory and easily handled without damage until ready for use. The manufacture of the sandwiched photoresist element is easily carried out with high precision on the continuous web coating machinery well known in the photographic manufacturing industry.

When it is desired to image a perforated element, the invention provides a method of laying down a resist without plugging the perforation holes as would be the case with liquid coatings. This is important where the holes are used for making soldered connections.

Coatings of the photopolymerizable composition on its supporting film can be made on precision continuous web coating machinery capable of highly uniform application over large areas. Dryers can remove all solvents from the coatings before the web is wound up. These operations, if carried out under clean conditions, especially if a cover film is laminated to the photopolymerisable layer, can produce extremely high quality, dirt-free photopolymerisable layers which are completely protected in the sandwich form until use. This also facilitates thorough inspection during manufac-

ture. To make a resist image on, for example, a metal support such as copper, it is only necessary to strip off the laminated cover film and laminate the uncovered surface of the photopolymerisable layer to the metal support. The layer is still protected from lint, dust and other kinds of harmful dirt as well as from abrasion or scratches by the original support film. At the same time, it can be easily exposed through the film. The whole operation of the process of the invention is much less time-consuming and much simpler to carry out by the user than are the processes of the prior art.

The invention will be further illustrated by the following Examples, wherein the percentages are by weight.

EXAMPLE I

A solution was prepared of the following ingredients:

Methyl methacrylate/itaconic acid copolymer (19/1)	24.5 g.
Pentaerythritol triacrylate (Example 1 of Specification No. 1055196)	7.8 g.
2-t-Butyl anthraquinone	0.30 g.
Crystal Violet (C.I. Basic Violet 3)	0.06 g.
Methyl ethyl ketone to make	120.0 g.

The solution was coated onto a 0.002 mm. thick polyethylene terephthalate film support and dried in air. The dry thickness was about 0.013 mm.

A piece of copper clad, epoxy-fibre glass board was cleaned by scouring with an abrasive cleaner, swabbing and thoroughly rinsing in water. It was then given a 20 second dip in a dilute hydrochloric acid solution (2 volumes water+1 volume conc. hydrochloric acid), a second rinse with water and then dried with air jets.

The coated support was laminated to the clean copper with the surface of the photopolymerisable layer in contact with the copper surface. The lamination was carried out with the aid of rubber covered rollers operating at 120°C. with a pressure of 0.54 kg. per lineal cm. at the nip, at a rate of 61 cm. per minute. The resulting sensitized copper clad board protected as it is by the polyester film support, could be held for later use, if need be. Actually it was exposed to light through a high-contrast, transparency image in which the conducting pattern appeared as transparent areas on an opaque background. The exposure was carried out by placing the sensitized copper clad board (with its polyester film still intact) and the transparency into a photographic printing frame. The exposure was for a period of 5 seconds to a 2500 watt, 45-ampere carbon arc at a distance of 25.7 cm. The polyethylene terephthalate support film was peeled off and the laminate was washed with carbon tetrachloride to remove the unexposed areas of the photocopolymerisable layer. A dyed resist image remained adhered to the copper surface. Etching of the non-imaged areas of the copper was carried out with 0.5 molar ammonium persulphate solution which removed the copper from the fibre glass support leaving the copper image covered with dyed resist in the light-exposed areas. The resist was removed from the copper by washing with methyl ethyl ketone to provide a high quality printed circuit board.

EXAMPLE II

A solution was prepared from the following ingredients:

Methyl methacrylate/methacrylic acid copolymer (9/1)	306.0 g.
Pentaerythritol triacrylate (See Example I)	82.5 g.
Ethyl Violet (C.I. 42600)	0.25 g.
9,10-Phenanthrenequinone	2.5 g.
Acetone to make	750.0 g.

This solution was coated on 0.003 mm. thick polyethylene terephthalate film and dried in air to give a photopolymerisable layer about 0.013 mm thick. A sheet of cold-rolled steel was cleaned with a degreasing solvent, a detergent and an abrasive cleaner, washed with water, and finally rinsed with acetone. The photopolymerisable layer on its polyethylene terephthalate film support was laminated to the cleaned surface of the steel using heated pressure rollers at a temperature of 105°C. and at 152 cm. per minute with 0.36 kg. of force per lineal cm. of nip. The resulting photosensitive element was exposed for 3 minutes through a high contrast line (text) transparency as described in Example I. After exposure, the polyethylene terephthalate film was peeled off and discarded. The coated steel sheet was then washed in carbon tetrachloride to remove the unexposed areas of the photopolymerisable layer. After stand-

ing for 30 minutes, the imaged steel sheet was immersed in 30% nitric acid until 0.3 mm of the steel had been etched away in areas not covered by the resist. This resulted in a steel relief image which was highly useful as a printing plate.

EXAMPLE III

A solution was prepared as follows:

Binder solution *	306.3 g.
Pentaerythritol triacrylate	82.5 g.
Ethyl Violet dye	0.25 g.
2-t-Butyl anthraquinone	2.5 g.
Acetone to make	750.0 g.

* 24.7% solution of methyl methacrylate/methacrylic acid copolymer (90/10) in methyl ethyl ketone.

This solution was coated onto 0.003 mm. thick polyester film and dried to provide a photopolymerisable layer. Dry thickness was 0.01 mm.

A glass microscope slide was washed in detergent solution, rinsed in distilled water and then ethanol, and dried. The layer was then laminated to the glass at 35°C., applying finger pressure. The element was then exposed for 3 minutes through a high-contrast transparency to light from a carbon arc as in Example I.

After exposure, the polyester film was peeled from the surface and the image was developed by washing in carbon tetrachloride. The polymer resist remained in the areas which had been exposed. The resist-bearing slide was next immersed in 48% hydrofluoric acid solution for 30 seconds and immediately washed in running water. This treatment caused the etching to extend about 0.05 mm. into the glass slide in areas not protected by the resist. The polymeric resist was next removed by swelling it in methylene chloride and swabbing clean. An etched relief image remained in the glass slide.

EXAMPLE IV

A photopolymerisable composition comprising 54 parts polymethylmethacrylate, 35 parts of a diacrylate of a polyethylene glycol having a molecular weight of 300, 5 parts triethylene glycol diacetate, 5 parts 2-t-butyl anthraquinone, 0.3 part 2,2'-methylene bis-(4-ethyl-6-t-butyl phenol) and 0.7 parts Victoria/Pure Blue BO (C.I. Basic Blue 7) were dissolved in trichloroethylene was coated on 0.025 mm untreated polyethylene terephthalate film and allowed to dry to provide a photopolymerisable layer. The layer was laminated to clean copper clad circuit board at a speed of 2.54 cm per second and a roll temperature of 120°C to yield a sensitized photoresist board. The sensitized image was exposed for 40 seconds on a "Nu arc" Plate Maker, Flip Top Model FT-26M-2 carbon arc. The polyethylene terephthalate film was stripped off and the unexposed areas were dissolved in methyl chloroform to yield a resist image on the surface of the copper. The resist image was found satisfactory for ferric chloride etching and gave a printed circuit directly. It was also suitable for a solder electroplating resist allowing imagewise electroplating of lead-tin alloy. It was also suitable for copper plating and copper pyrophosphate plating baths without underplating or nodule formation.

EXAMPLE V

A similar composition to Example IV was prepared except 35 parts triethylene glycol diacrylate was used in place of the polyethylene glycol diacrylate. The results obtained with this material were very similar to those obtained in Example IV except the photospeed was different. An exposure of 15 seconds was all that was required for this composition. The results of ferric chloride etching, solder plating and copper pyrophosphate plating were similar to results obtained in Example IV.

EXAMPLE VI

A similar composition to Example IV was made replacing the polyethylene glycol diacrylate with 35 parts of the triacrylate of oxyethylated trimethylolpropane (average mol. wt. 1000) as described in U.K. Patent Specification No. 1,055,198. This composition was used on copper clad board in the manner described in Example IV and the resist image could be etched in ferric chloride, solder plated in a lead-tin fluoroboric acid bath or copper plated in a copper pyrophosphate bath. The results were as follows:

Photospeed — this film required 75 seconds to give a good image. At this exposure solder plating was excellent.

Copper plating was also satisfactory.

EXAMPLE VII

A photopolymerisable composition comprising 50.1 parts of a copolymer of 50% methylmethacrylate and 50% butylmethacrylate, 38.1 parts pentaerythritol triacrylate, 5.4 parts triethylene glycol diacrylate, 5.4 parts 2-tert-butyl anthraquinone, 0.3 part 2,2'-methylene bis-(4-ethyl-6-t-butyl phenol) and 0.7 part of Victoria Pure Blue BO dissolved in trichloroethylene was coated on 0.025 mm. untreated polyethylene terephthalate film and dried to a thickness of 0.0125 mm to provide a photopolymerisable layer. The photopolymerisable layer was laminated through pressure rolls at 120°C. at a speed of 2.54 cm per second to yield a sensitized copper clad printed circuit board. An exposure of 80 seconds on the Flip Top carbon arc of Example IV was sufficient to yield a satisfactory photoresist image on the copper. The polyethylene terephthalate film was stripped off and unexposed areas of the photopolymerisable layer were removed. The resist imaged board was then etched in ferric chloride and yielded an excellent printed circuit. Similarly when the resist imaged copper was electroplated in a lead-tin fluoroborate bath no underplating or nodule formation resulted. Similar results were obtained in a copper pyrophosphate plating bath at 30 amps. per 929 sq. cm. and 55°C.

It is possible to substitute polyvinylacetate, 80/10/10 ethylene terephthalate/ethylene isophthalate/ethylene sebacate terpolymer, polystyrene or styrene/isobutylene copolymers for the copolymer binder in the composition described above with equivalent results.

EXAMPLE VIII

A composition comprising 54 parts polymethylmethacrylate, 30 parts triethylene glycol diacrylate, 10 parts triethylene glycol diacetate, 5 parts 2-tert-butylanthraquinone, 0.7 part 2,2-methylene bis-(4-ethyl-6-t-butyl phenol), 3 parts Victoria Blue BO dissolved in trichloroethylene and coated as a photopolymerisable layer to a dry thickness of about 0.0125 mm on a film of polyethylene terephthalate. The layer was laminated to a clean copper surface using heated pressure rolls at 120°C. to yield sensitized copper boards. Similar results were obtained when the layer was laminated to clean copper at room temperature showing that heat was not necessary for good lamination. The resist was exposed for 40 seconds on the Flip Top carbon arc described in Example IV. The polyethylene terephthalate film was removed and the imaged layer was developed in a recirculating spray of an azeotropic mixture of perchloroethylene and isobutyl alcohol at 25°C. This solvent readily dissolved the unexposed areas leaving a resist image on the surface of the copper. The resist image so produced was satisfactory for solder plating at 15 amps. per 929 sq. cm. for 15 minutes yielding no nodule formation, underplating or resist embrittlement. Excellent results were obtained. This image was also satisfactory for plating in copper pyrophosphate. The resist was also satisfactory for eaching printed circuits in ferric chloride. The resist image was also satisfactory as a molten solder resist. In this technique the resist imaged copper board was fluxed with white rosin in isopropyl alcohol, the rosin allowed to dry and then the board immersed in molten solder at 210°C. for 7 seconds and slowly withdrawn. The copper exposed was readily we with the molten solder and the resist protected the copper from being solder plated. This is an excellent example of how a wave soldering machine and this photoresist can be used to rapidly apply solder imagewise to a copper board.

EXAMPLE IX

A composition comprising 54 parts polymethylmethacrylate, 35 parts 1,4-butylene glycol diacrylate, 5 parts triethylene glycol diacetate, 5 parts 2-tert-butylanthraquinone, 0.7 part 2,2'-methylene bis-(4-ethyl-6-t-butyl phenol), 0.3 part Victoria Pure Blue BO dissolved in trichloroethylene was coated as a photopolymerisable layer on a 0.025 mm thick polyethylene terephthalate film to a dried thickness of 0.0125 mm. The coating after drying was laminated to copper clad circuit boards using hot roll machines at 120°C in a web speed of 2.54 cm per second. Exposure of at least 30 seconds on the Flip Top carbon arc were necessary for complete image formation. After exposure, the polyester film was removed and the image developed in a recirculating spray comprising 70 wt. % perchloroethylene, 30 wt. % isobutyl alcohol. This resist image on copper was suitable for ferric chloride etching. This composition was also found suitable for application to aluminum. After imaging, the resist image

was baked for 15 minutes at 200°C. The aluminum was then etched in hot 20% sodium hydroxide solution to yield an etch depth of 0.1 mm in 50 minutes.

EXAMPLE X

A composition similar to the one described in Example IX was prepared, except that glycerol trimethacrylate was used instead of 1,4-butylene glycol diacrylate. This film composition could be laminated at room temperature or 120°C. The results obtained were similar to Example IX on copper and on aluminum in terms of photospeed, resolution and dielectric characteristics. The etching of aluminum was significantly better than when the monomer in Example IX was used.

EXAMPLE XI

A composition comprising the same ingredients as in Example IX was prepared except the monomer was tetraethylene glycol dimethacrylate. The composition was coated as in Example IX and yielded similar results.

EXAMPLE XII

A composition similar to Example IX was prepared but in this case the monomer trimethylolpropane trimethacrylate was used. The results of this composition coated in a similar fashion and laminated to copper showed a photospeed of 120 seconds on the Flip Top carbon arc described in Example IV and good adhesion after exposure. This composition could not be room temperature laminated but could be readily laminated with roll temperatures of 120°C. Results on aluminum were the same as in Example X.

EXAMPLE XIII

A composition similar to Example IX, except 1,3-butylene glycol dimethacrylate was used as the monomer, was prepared and coated as in that Example and evaluated on copper and aluminum. Exposure required for this composition was about 60 seconds on the Flip Top carbon arc. Results on etching and electroplating were comparable to Example IX.

EXAMPLE XIV

A composition was prepared similar to that of Example IX except tetramethylethylene glycol dimethacrylate was used as the monomer with similar results. When this composition was laminated to glass, exposed for 40 seconds on the Flip Top carbon arc, a suitable image was obtained with good adhesion to the glass. If the image was post-baked after development for 10 minutes at 180°C., the resist image was suitable for etching in 48% hydrofluoric acid. If different colour dyes or pigments were put into this formulation, coloured glass slides could be made directly from this composition.

EXAMPLE XV

Using the composition described in Example V, the coating was laminated to glass, exposed for 40 seconds on the Flip Top carbon arc, developed in 70% perchloroethylene, 30% isobutyl alcohol to remove the unexposed resist, and the results obtained were similar to the glass results in Example XIV. However, best etching results were obtained when 20% hydrofluoric acid was used rather than 48%.

EXAMPLE XVI

A composition was prepared comprising 49 parts polymethylacrylate, 40 parts 1,3-butylene glycol diacrylate, 5 parts triethylene glycol diacetate, 5 parts 2-tert-butylanthraquinone, 0.7 part 2,2-methylene bis-(4-ethyl-6-t-butyl phenol), 0.3 part Victoria Pure Blue BO. A resist film prepared as in Example IV allowed room temperature lamination when applied to a substrate through pressure nip rollers. The results obtained were very similar to those described in Example V.

EXAMPLE XVII

A composition similar to the one described in Example XVI was prepared except neopentylglycol diacrylate was used as the monomer in place of 1,4-butylene diacrylate. The composition, after being coated and laminated as described above, showed a photospeed on copper of 40 seconds on the Flip Top carbon arc. The exposed adhesion to copper was adequate. The developer, however, was trichloroethylene because this composition was not totally soluble in the usual perchloroethylene/isobutyl

alcohol solvent. After development the images were found satisfactory as ferric chloride etching resists.

EXAMPLE XVIII

A composition was prepared which was basically the same as in Example IX except the monomer was pentaerythritol triacrylate instead of 1,4-butylene glycol diacrylate. The composition was applied to a polyester support as in Example IX to provide a photopolymerisable layer of dry thickness 0.0125 mm. The layer was laminated through a set of hot rolls at 120°C. at 2.54 cm per second to an aluminum substrate covered with "Nichrome" (Registered Trade Mark) and gold. After lamination the sample was heated for 2 minutes at 165°C. and cooled. The sample was then exposed with a 1200 watt mercury source collimated with a 3 inch diameter black tube 26 inches long. The exposure required was 8 seconds and, after removal of the support, the image was developed for 30 seconds in methyl chloroform which removed the unexposed areas of the layer leaving an insoluble resist image on the gold substrate. After development the image was baked for 10 minutes at 180°C., it was then etched for 2 minutes in one normal KI/I etchant, which easily removed the exposed gold which was not protected by the resist. The results were excellent.

WHAT WE CLAIM IS:—

1. A process for the localised permanent modification of a solid surface in predetermined areas only which comprises laminating at a temperature up to 150°C. directly to the surface a dry, flexible photosensitive layer which is coated on a flexible polymeric film support towards which it has low to moderate adhesion, the photosensitive layer consisting of a photopolymerisable composition comprising an addition polymerisation initiator activatable by actinic light and a photopolymerisable compound which contains less than 10 ethylenically unsaturated groups per molecule, exposing the photosensitive layer imagewise to actinic radiation to form a polymer image therein either before or after removal of the support from the photosensitive layer, removing the unexposed areas of the photosensitive layer by means of a liquid to leave a resist image on the solid surface and subjecting the surface carrying the resist image to an etching or plating treatment whereby the unprotected areas thereof are permanently modified.

2. A process according to claim 1, wherein the ethylincally unsaturated groups are vinyl or α-methylvinyl groups.

3. A process according to claim 1 or 2, wherein the photopolymerisable compound contains from 1 to 6 acrylate or methacrylate ester groups per molecule.

4. A process according to claim 3, wherein the photopolymerisable compound is a diacrylate or dimethacrylate of an alkylene glycol or polyalkylene glycol or an acrylate or methacrylate of pentaerythritol or dipentaerythritol.

5. A process according to claim 3, wherein the photopolymerisable compound is one of the acrylates or methacrylates specifically mentioned in any one of Examples I—XVIII.

6. A process according to any one of the preceding claims, wherein the polymerisation initiator is a polynuclear quinone having two intracyclic carbonyl groups attached to intracyclic carbon atoms in a conjugated carbocyclic ring system.

7. A process according to any one of the preceding claims, wherein the surface to which the photosensitive layer is laminated is of an inorganic material.

8. A process according to claim 7, wherein the surface is of copper, anodized aluminium or glass.

9. A process according to any one of the preceding claims wherein the film support transmits radiation to which the layer is photosensitive.

10. A process according to claim 9, wherein the film support is removed from the layer after exposure.

11. A process according to claim 9 or 10, wherein the support is a polyethylene terephthalate film.

12. A process according to any one of claims 1 to 8, wherein the support is opaque to radiation to which the layer is photosensitive and is removed from the layer before exposure.

13. A process according to any one of the preceding claims, wherein a protective cover sheet is initially laminated to the face of the photosensitive layer to be laminated to the surface, and the cover sheet is removed before the layer is laminated to the surface.

14. A process according to claim 13, wherein the cover sheet is a polyethylene film.

15. A process according to any one of the preceding claims, wherein the resist is subsequently removed from the unmodified areas of the surface.

16. A process for the localised permanent modification of a solid surface according to claim 1 substantially as hereinbefore described.

17. An element comprising a surface carrying an image and obtained by a process claimed in any one of claims 1—16.

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